ABSORPTION SPECTRA STUDIES OF ORGANIC NITRO COMPOUNDS

BY

ISAAC FELDMAN

B. S., The George Washington University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

Because of the speed of the neutralization of nitroparaffins, kinetic studies have been conducted, heretofore, only at temperatures near 0°C. The most direct physical approach previous to this investigation was the conductimetric method (1, 2).

Since absorption spectroscopy is an even more direct and a more sensitive method, this research was carried out with the primary purpose of obtaining kinetic data for the neutralization at room temperatures.

It was also hoped that evidence could be obtained concerning the complete reversibility of the reaction (1) and the postulated existence in acid solution of two forms of a nitroparaffin, the nitro form, R_2CHNO_2, and the aci form, $R_2C = NOOH$ (3).

Discussion of Results

Ultraviolet absorption spectra of sodium hydroxide solutions of nitromethane (4), nitroethane, and 2-nitropropane revealed that the wave lengths of the absorption maxima characteristic of the ion forms decrease as methyl substitution increases. This trend was explained by postulating that the excited state of the ion is $R_2C^- - N^+O O^-$.

The basic routine of the rate experiments consisted of measuring the optical density, with a Beckman Photoelectric Quartz Spectrophotometer, at 2450 A of the reacting solution at measured time intervals. Since the absorption at 2450 A by the nitro form was negligible compared to that of the ion form, the concentration of the ion form produced in a given time was proportional to the optical density of the

solution. The success of this absorption method depended upon the fact that the relatively high molar extinction coefficient ($E = 1950$) of the ion form at 2450 A allowed the use of 2-nitropropane concentrations which were sufficiently small (5×10^{-4}M) to cause the neutralization to proceed at a measurable rate in the temperature range, 20°C. to 30°C.

To conduct the kinetic study of the reaction of 2-nitropropane with sodium hydroxide it was necessary to maintain a nitrogen atmosphere and to use alkali-resistant flasks. If these precautions had not been taken, the reaction would have proceeded to an extent of only 75% and calculations would have been inaccurate, since the initial hydroxyl ion concentrations were only about 5×10^{-4}M. This reaction was shown to be second order, the specific rate constants at 20°C., 25°C., and 30°C. being given by the equation:

$$\log_{10} k_{sec} = \frac{-3780}{T} + 12.26$$

The energy of activation was, accordingly, 17,300 calories/mole.

In phosphate buffer solutions at constant pH the neutralization of 2-nitropropane followed the reversible first order equation. Since the same initial concentration of nitroparaffin, and of the ion form because the reaction had proceeded to an extent of about 3% in the stock water solution of nitroparaffin, was used at each pH, the determination of the initial rate at different pH's effectively gave the rate of neutralization as a function of factors which depended on the pH, that is, as if the nitropropane and ion form concentrations remained constant while factors determined by the pH were changing. It was shown that in phosphate buffers the rate of neutralization of the nitro form of 2-nitropropane is given by the expression:

$$\frac{dX}{dt} = k_{OH}(OH)\ (nitro) + k_{HPO_4}(HPO_4)\ (nitro) - k_{H_3O}(H_3O)\ (ion) - k_{H_2PO_4}(H_2PO_4)\ (ion)$$

This supports the belief that the forward reaction is produced by bases in general (5) and that the reverse reaction is brought about by acids in general (6).

Attempts to completely reverse the ionization of the nitro form by adding acid to a solution of the sodium salt were not successful.

No evidence was obtained concerning the existence of the aci form of a nitroparaffin. It is believed, however, by this investigator that, because of the instability and the unknown absorption spectrum of the aci form even if it should exist, and because of the necessity of making a new setting of the dials of the instrument for each wave length studied, the Beckman Spectrophotometer can not be used to obtain such information.

An attempt was made to explain the failure of the rate-equilibrium parallelism of nitroparaffins by postulating that methyl substitution, which slows down the neutralization reaction, tends to prevent the re-attachment of the proton to the ion.

A possible mechanism for the neutralization was offered. It is:

nitro $\rightarrow$ intermediate hybrid ion $\rightarrow$ stable hybrid ion

Both resonance hybrid ions have the same contributing end states (7), $R_2C^- - N^+OO^-$ and $R_2C = N^+O^-O^-$, but the latter structure contributes more to the stable hybrid ion than it does to the intermediate ion.

BIBLIOGRAPHY

1. Maron, S. H., and LaMer, V. K., J. Am. Chem. Soc., **60**, 2588 (1938).

2. Maron, S. H., and LaMer, V. K., Ann. New York Acad. Sciences, vol. XXXIX, 355 (1940).

3. Turnbull, D., and Maron, S. H., J. Am. Chem. Soc., **65,** 212 (1943).

4. Kortum, G., Z. Physik. Chem., **43,** 271 (1939).

5. Pedersen, K. J., Kgl. Danske Videnskab. Selskab, Math.-fys. Med., **12,** 1 (1932) ; Chem. Zentr., **103,** 2950 (1932).

6. Junell, R., Svensk Kem. Tid., **46,** 125 (1934).

7. Kornblum, N., Lichtin, N. N., Patton, J. J., and Iffland, D. C., J. Am. Chem. Soc., **69,** 307 (1947).

VITA

The author was born March 6, 1918, in Washington, D. C., and received his primary and secondary education in the public schools there, being graduated from the Eastern High School in 1935. He was granted the degree of B. S. in Chemistry by The George Washington University in June, 1941, and at that time won the Alpha Chi Sigma Senior Award, The American Institute of Chemists Award, and the Willie Fitch Prize in Chemistry. He was an Assistant in Chemistry at that university from September, 1939, to August, 1942, and pursued graduate studies there in Bacteriology and Chemistry from September, 1941, to August, 1942. After serving for six months as a Civilian Instructor in the United States Army Air Forces Technical School at Scott Field, Illinois, he returned to The George Washington University as an Instructor in Chemistry, which position he held from February, 1943, to June, 1944, and continued his graduate work there part-time until October, 1944.

The writer entered the Graduate School of the University of Illinois in October, 1944. He held a teaching assistantship in the Analytical Chemistry Division from that time until February, 1947, and a University of Illinois Fellowship from February, 1947, through September, 1947.

He holds memberships in The American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Pi Mu Epsilon.

He is junior author of the paper:

Rodebush, W. H., and Feldman, I., J. Am. Chem. Soc., **68,** 896 (1946).

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